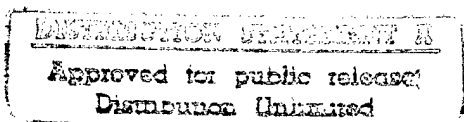


Organo-Aluminate Polymeric Materials as Advanced Erosion/Corrosion Resistant Thin Film Coatings

**Year 1
Quarterly Report No. 4
June 19, 1997**

**for Dr. Harold Guard (ONR) and Dr. Steven Wax (DARPA)
Contract #N00014-96--0147**



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Title: *Organo-Aluminate Polymeric Materials as Advanced Erosion/Corrosion Resistant Thin Film Coatings*

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Proprietary Sections

The information contained on pages 6-11 is considered proprietary. TDA and its team members will file invention disclosures with the Office of Naval Research on the materials and technologies developed during the program and will also file patent applications for the technologies described on pages 6-11 when development of the technologies are fully reduced to practice.

1. Executive Summary (Fourth Quarter, Year One)

The goal of this three year DARPA project is the development, formulation and production of chromate-free alumoxane-based durable coatings that can provide a high level of corrosion resistance with low VOC and HAP emissions. The coating system is being designed for repair and maintenance of corrosion/mission coatings on existing DoD aircraft inventories. In the fourth quarter of the first year of this DARPA project, we have focused our efforts on the synthesis of alumoxane-epoxies that can be cured at room temperature since it is not feasible to heat the entire aircraft and higher

temperatures can significantly accelerate metal fatigue of the advanced aluminum alloys. Since room temperature cures of epoxies are generally carried out using aliphatic amines or polyamides we have prepared an alumoxane with terminal amine functional groups. The amine functionalized carboxylic acid used to prepare the alumoxane was 2,6-diaminohexanoic acid (the common name is lysine which is available in large quantities for ~\$1.00/lb). When attached to the boehmite particle the two terminal amines can become incorporated directly into the growing epoxy resin chain. During this quarter we have also been evaluating methods for scale-up of the syntheses of the carboxylato-alumoxanes so that more rapid evaluations of selected epoxy-alumoxane coating formulations for corrosion resistance can be carried out. We have identified two potential scale-up routes (the use of aluminum sec-butoxide or Condea-Vista Dispal™) to prepare the nano-sized boehmite that is used to prepare the carboxylato-alumoxanes. We have demonstrated that a synthetic route using the aluminum sec-butoxide procedure can be scaled up and are awaiting delivery of the Dispal™ to evaluate the second approach. We have also begun to characterize the mechanical properties of the alumoxane-epoxies and found that ~100% increase in the strength of the epoxies can be achieved by addition of the alumoxane epoxies. The dimensional properties of the epoxy-alumoxanes are also significantly improved. Professor Barron's group is developing methods to follow the cure rates of the epoxies and characterize the alumoxane-epoxy/aluminum interface. Professor Stoffer's group is in the process of developing epoxy-alumoxane coating formulations using the carboxylato-alumoxanes.

2. Project Description

The primary goal of the DARPA program is the development of carboxylato-alumoxane based coating systems for repair and maintenance of DoD aircraft coatings. The proposed coating systems can potentially offer improved durability and corrosion protection, while avoiding the use of chromates and minimizing the emissions of both volatile organic compounds (VOCs) and hazardous air pollutants (HAPs).

The coating system is based on the development of carboxylato-alumoxane precursors for fabrication of corrosion resistant oxide barrier layers and alumoxane-epoxy based primer coats. Carboxylato-alumoxanes are low-cost nano-composite materials prepared from the reaction of carboxylic acids and the mineral boehmite ($\text{AlO}[\text{OH}]$), ~\$1/lb). The carboxylic acids are bound to the surfaces of the boehmite particles (Figure 1). The alumoxanes can be

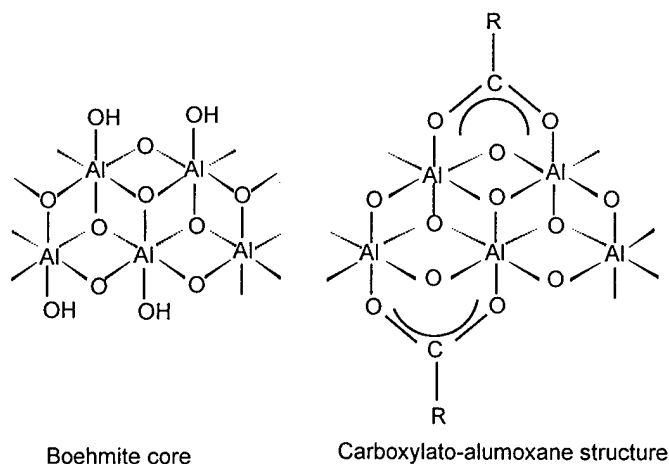


Figure 1. Comparison of the core structures of boehmite and the carboxylato-alumoxane.

directly bonded into polymer matrices by the use of carboxylic acids that have the appropriate functional groups (i.e. -OH, -NH₂, etc). The bonding of the particles to the polymer matrix reduces the voids inherent in filled polymers at the interface of hydrophilic fillers and hydrophobic polymers. The "filled" alumoxane-epoxies potentially offer better barrier properties and improved mechanical properties over current epoxy corrosion coatings.

The covalently bound carboxylic acid groups also impart a unique reactivity to the coated boehmite particles. Previous work at TDA and by Professor Barron's group has shown that the attached carboxylic acids allow room temperature metal-exchange reactions to be carried out with the carboxylato-alumoxanes (Kareiva et al. 1996). We are using this unique property of the carboxylato-alumoxanes to prepare cerium and molybdenum exchanged precursors that can be used to prepare corrosion resistant Ce/Mo-doped aluminum oxide barrier layers on aluminum substrates by plasma spraying techniques. The corrosion-resistant oxide barrier will then

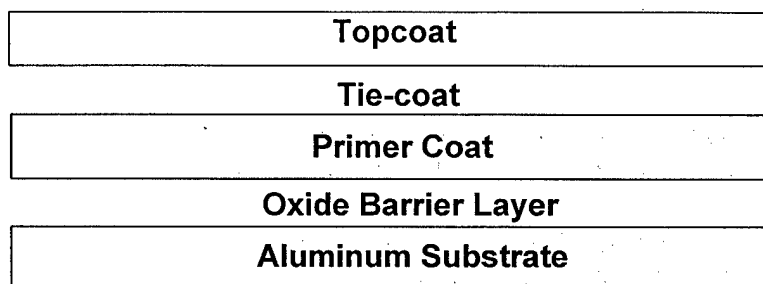


Figure 2. Schematic of coating system for aerospace applications.

be coated with a mechanically strong epoxy-alumoxane primer coat. These materials form the basis of a system that will eventually include high performance urethane-alumoxane topcoat (Figure 2).

3. Summary of The First Year's Work

As discussed in the previous section, the goal of this DARPA sponsored project is the development and testing of alumoxane based epoxy coatings for corrosion and erosion control on high performance (Al-2024-T3, Al-7075-T6) aircraft aluminum. In the first year of the project we have prepared a range of functionalized alumoxanes, identified routes to incorporate the alumoxanes into epoxies into a range of thermoset polymers (e.g. epoxies, urethanes, polyamides, polyimides, etc.), and developed production techniques to prepare one to ten pounds of alumoxanes at a time.

New carboxylato-alumoxane precursors (for preparation of alumoxane-epoxy resins) prepared during the first year (by the reaction of boehmite with carboxylic acids) included alumoxanes containing -OH functional groups (4-hydrobenzoic acid, 3,5-dihydroxybenzoic acid, 4,4-bis(4-hydroxyphenyl)valeric acid, dimethylolpropionic acid, and gluconic acid), -NH₂ functional groups (4-aminobenzoic acid, 6-aminoheptanoic acid and 2,6-diaminoheptanoic acid), and -CH=CH₂ functional groups (acrylic acid, methacrylic acid, and ricinoleic acid).

During the first year's efforts we also verified that the functionalized alumoxanes could be incorporated into thermoset polymer resins. We have prepared epoxy-alumoxane resins, urethane-alumoxane resins and acrylic (or methacrylic) alumoxane resins. We are currently scaling up production of the alumoxanes so that coating formulation efforts can be carried out and the corrosion resistance evaluated. For the coating formulation efforts we are working with Professor Jim Stoffer (University of Missouri-Rolla) and a local commercial epoxy formulator (Epoxy Formulations, Inc.). Professor Barron's group is developing methods to characterize the cure kinetics of the epoxy-alumoxanes and for characterization of the aluminum/alumina/epoxy-alumoxane interface.

4. Current Research Results (March 19, 1997 - June 19, 1997)

4.1.1. Scale-up of Production for Alumoxane Resin Precursors

The synthesis of carboxylato-alumoxanes developed by Professor Barron's group was initially based on the reaction of carboxylic acids with pseudoboehmite in xylenes at temperatures around 130°C (Apblett et al. 1992, Landry et al. 1995). This approach has some undesirable features such as the use of large quantities of organic solvents and the relatively long time period (3-4 days) required to convert the pseudoboehmite to the nano-sized alumoxane particles. During the first year of the DARPA project, TDA and Professor Barron's group developed syntheses of carboxylato-alumoxanes using water as the reaction solvent. Many of the resulting materials that were synthesized were also found to be water soluble (or dispersible), thereby allowing the use of water-borne (i.e. low VOC) formulations for the potential aircraft coatings.

Although Professor Barron's group has demonstrated that the reaction of acetic acid with the Catapal boehmite in water is a rapid procedure for the synthesis of nano-sized acetato-alumoxanes, the synthesis of functionalized (-OH, -NH₂ etc.) alumoxanes still requires 3-4 days to completely convert the pseudoboehmite (typically Catapal A, B or D, Condea-Vista Company) particles to the nano-sized carboxylato-alumoxanes. This extended reaction time is presumably a result of the need to break down the larger boehmite aggregates to smaller particles whose surfaces are coated with the functionalized carboxylic acids. If the boehmite particles were already nanometer size prior to reaction of with the carboxylic acids, then the synthesis time (and the labor costs) could be significantly reduced.

We therefore are evaluating two approaches for the rapid production of larger scale quantities of the carboxylato-alumoxanes so that production and fabrication of the epoxy-alumoxane coatings can be carried out on an accelerated basis during the second year of the project. In the first approach we have evaluated the sol-based pseudoboehmite synthesis approach described by Clark and coworkers (Clark et al. 1989). In this approach, the aluminum sec-butoxide (ASB) was hydrolyzed in water at 80°C and then peptized by the addition of aluminum nitrate. This procedure results in the formation of 30-70 nm pseudoboehmite particles. To the aqueous pseudoboehmite

sol we then added the carboxylic acids. After several hours of stirring, the reaction is complete and the carboxylato-alumoxane can be separated from the mixture and purified. We have identified a low-cost large-volume producer for the ASB. Chattem Chemicals offers ASB in quantities from 5 gallon pails to 55 gallon drums at prices of \$2.35/lb and \$2.11/lb respectively. This route offers a rapid synthetic route to nano-sized pseudoboehmite particles that react rapidly with carboxylic acids to form the desired functionalized alumoxanes. Due to the higher cost of the ASB (and loss of weight on transformation to pseudoboehmite) the resulting nano-size pseudoboehmite particles have an estimated raw materials cost of \$8.50/lb to \$10.00/lb (compared to raw materials cost of \$2.50-\$3.50/lb for the Catapal materials).

We have recently met with a technical sales manager from Condea-Vista (Dr. Scott Leigh). He has suggested that we evaluate the use of Condea-Vista's Dispal boehmite sols. One material (Dispal™ 23N4-20) is an aqueous sol mixture containing 90 nm pseudoboehmite agglomerates. From our discussions with Dr. Leigh, we anticipate that we can use a high shear mixer to further disperse the 90 nm boehmite agglomerates prior to reaction with the carboxylic acids. Figure 3 shows a photo of the high shear reactor that TDA has recently purchased and will use to evaluate the Dispal-based precursor approach for scale-up of the alumoxane syntheses. In this approach we will heat the boehmite sol to 50 - 80°C and then begin stirring with the high shear stirrer. We will take samples of the stirred materials, and estimate the particle size using TDA's Malvern Mastersizer particle size analyzer. With the high shear stirrer still operating we will then add the carboxylic acids and continue stirring for several hours. Since Condea-Vista offers the Dispal materials in large quantities at

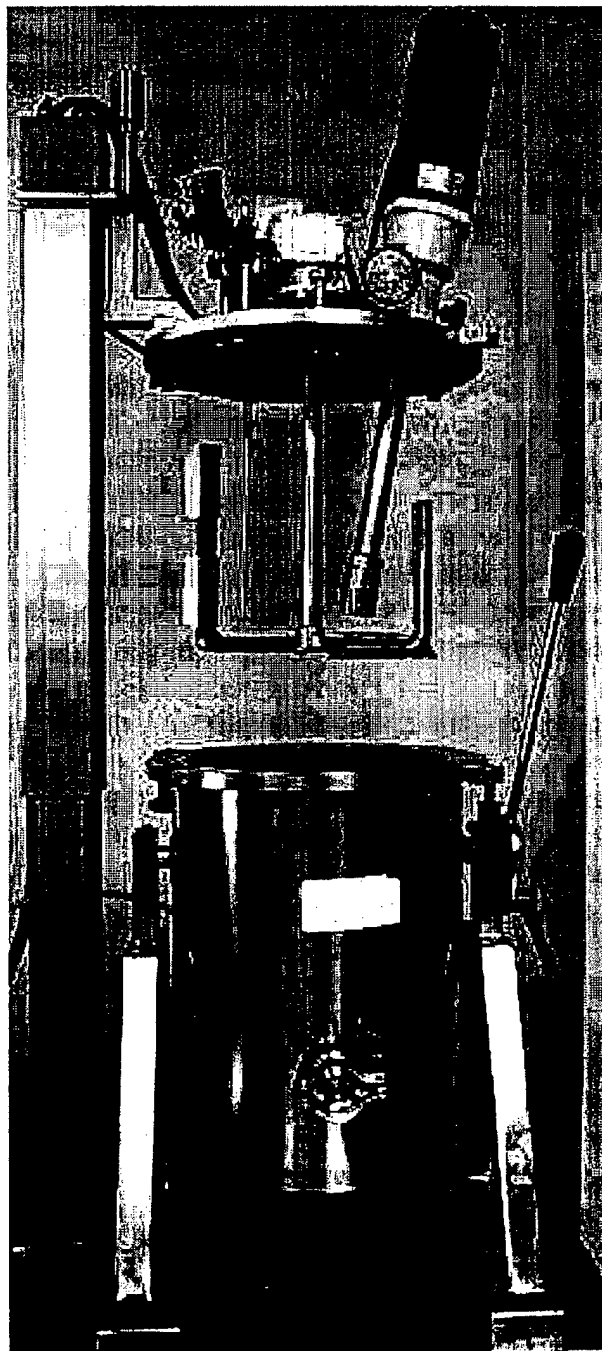


Figure 3. Photograph of 30 liter high shear reactor for alumoxane production.

reasonable prices (\$3/lb-\$4/lb) this may be a more cost effective route to production of functionalized alumoxanes for the epoxy-alumoxane coatings.

4.2. Fabrication of Room Temperature Curable Alumoxane Epoxies

In our early efforts to develop epoxy-alumoxane and urethane-alumoxane resins for fabrication of corrosion and erosion resistant coatings, we have prepared a number of OH functionalized alumoxanes. These materials were then incorporated into epoxy resins that were cured at 150°C-250°C. However, epoxy-based primer coatings for aircraft require room temperature cures since it is impractical to heat the entire aircraft. We have therefore focused our efforts on development of room temperature cure epoxy-alumoxane corrosion coatings.

To effect a room temperature cure for epoxy resins, aliphatic amines (primary or secondary) and polyamides are used. Following a brief examination of the *Chemical Marketing Reporter* we identified an aliphatic-amine-functionalized carboxylic acid that can be used to prepare the desired room temperature curable epoxy-alumoxane resins. The carboxylic acid is the amino acid lysine (2,6-diaminohexanoic acid). Lysine has several attractive attributes; it is available for ~\$1 per pound, it is difunctional so that the amine-terminated aliphatic chain can be incorporated into epoxy resin (thereby adding flexibility to the coating), and the terminal amines can undergo room temperature reaction with the epoxy-resin component. We therefore have developed a synthetic procedure for production of lysinato-alumoxanes.

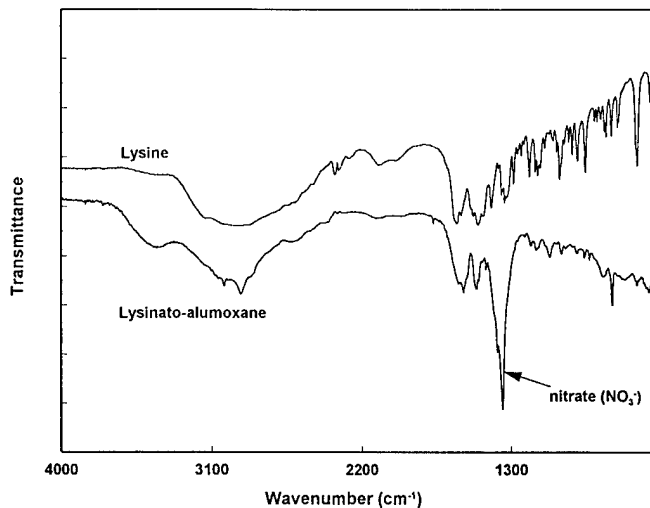
4.3. Synthesis of Lysinato-Alumoxanes

As discussed in Section 4.1.1, we have identified one scaleable production route that provides nano-sized pseudoboehmite particles for the subsequent production of the carboxylato-alumoxanes. We have carried out the synthesis of lysinato-alumoxane using this approach which is described in detail below.

To 3.2 liters of distilled water at 80°C we added 500g of ASB. To this mixture we then added 51.2g of aluminum nitrate. The mixture was then allowed to stir for several hours and the temperature then raised to 90°C to evaporate the butanol that was formed during the hydrolysis reaction. We then added 264.3 grams of lysine to the pseudoboehmite sol. After several hours of additional stirring, the water was removed and the resulting material was washed with ethanol and dried to give a white powder that is very soluble in water. The resulting material was characterized by FTIR, XRD, and TGA. The FTIR spectra of the lysinato-alumoxane (Figure 4) is typical of carboxylato-alumoxanes, showing the shift of the carboxylic acid stretch from that corresponding to a free carboxylate to a that corresponding to a bound carboxylate. The TGA spectra is also typical for a carboxylato-alumoxane with decomposition of the alumoxane occurring over a temperature range of 250 to 325°C and subsequent conversion of boehmite (via loss of water) to γ -alumina over the temperature range of

325 - 400°C. The powder XRD diffraction pattern showed features from both the boehmite core and the pendent lysine groups.

We have also found that mixtures of the lysinato-alumoxane and epoxies (such as DER 332) cure at near ambient temperatures. We are now attempting to formulate lysinato-alumoxane/epoxy resin mixtures for coating aerospace aluminum coupons for subsequent corrosion testing.



4.4. Characterization of Mechanical and Thermal Properties of Alumoxane Epoxies

Figure 4. Comparison of the FTIR spectra of lysine and lysinato-alumoxane.

During the fourth quarter of the DARPA program we have also begun to characterize the mechanical and barrier properties of the selected alumoxane materials. The results of the mechanical and thermo-mechanical tests are described below for epoxies prepared with the 4-hydroxybenzenato-alumoxane (HBA). We used this material for the initial studies of the mechanical and thermo-mechanical properties of the epoxy-alumoxanes because of our experience with preparing resins with the hydroxybenzenato-alumoxanes compared to the recently synthesized lysinato-alumoxanes. The epoxy-alumoxane resins were prepared by mixing Dow's DER 332 epoxy resin with Tone 0305 (a triol from Union Carbide) and with the hydroxybenzenato-alumoxane. As a control, a resin was prepared using 100 grams of the epoxy and 50 grams of the triol. We also prepared a resin formulation containing the epoxy plus the triol and HBA (100g DER 332, 50 grams triol and 25 grams of HBA) and a formulation containing the DER 332 resin and 35 grams of HBA. The three formulations were then cured at 140°C for six hours and then machined into the shapes required for testing. The results of the tests are discussed in the following sections.

4.4.1. Flexural Strength

Rectangular bars of the three epoxy formulations of approximate dimensions of 0.125 in x 0.125 in. x 1.2 in were machined and then subjected to a three point bend test to determine the flexural strength of the materials. In this test the sample is placed above two points and a third point is loaded onto the center of the sample. The load on the third point is increased until either the sample is fractured or bends to the maximum distortion that the instrument will allow. The results were very encouraging in that both of the alumoxane-epoxy composite materials formulated with the HBA-alumoxane exhibited better flexural strength than the epoxy alone (Figure 5). The epoxy alone had a strength of 51 MPa, the triol plus 14 phr HBA had a strength of 73 MPa and the 26

phr HBA-alumoxane cured epoxy (no triol) had a flexural strength of 97 MPa. These results indicate that the strength of the epoxy increases by almost 90% by the introduction of 26% (w/w) of the alumoxane.

These results, however, are obtained for epoxy alumoxanes whose cure rates and cross-link density have not been optimized. When one considers the formulation used in preparation of the 26 phr 4-HBA alumoxane cured system it is apparent that the alumoxane system is far from

optimized. The triol-free formulation consisted of 100g of the epoxy resin (with 5.9×10^{-3} epoxy equivalents per gram) and 35g of the HBA-alumoxane (with 5.0×10^{-3} hydroxyl equivalents per gram). In this formulation the epoxy thus is only slightly less than 30% cross linked. To completely cross link the epoxy resin would require a formulation with approximately 54 phr 4-HBAalumoxane. Furthermore, we observed a number of voids in the fracture surface of the test pieces. These defects undoubtedly played a role in initiating the fracture and limiting the strength of the epoxy-alumoxane materials.

4.4.2. TGA Analysis

The thermograms for the DER 332 epoxy resin cured with the triol, a mixture of the triol and HBA-alumoxane, and HBA-alumoxane without the triol are shown in Figure 6. It is evident from the thermograms that the initial weight loss of all of the samples occurs around 275 to 300°C. This indicates that the addition of the alumoxane does not affect the thermal-oxidative stability of the epoxy materials to any significant extent. However, as described in the next section the

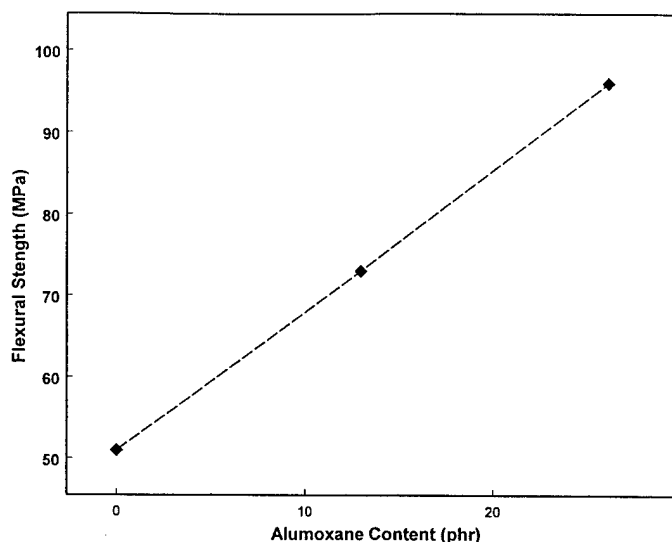


Figure 5. Flexural strength versus alumoxane loading for an alumoxane-epoxy polymer.

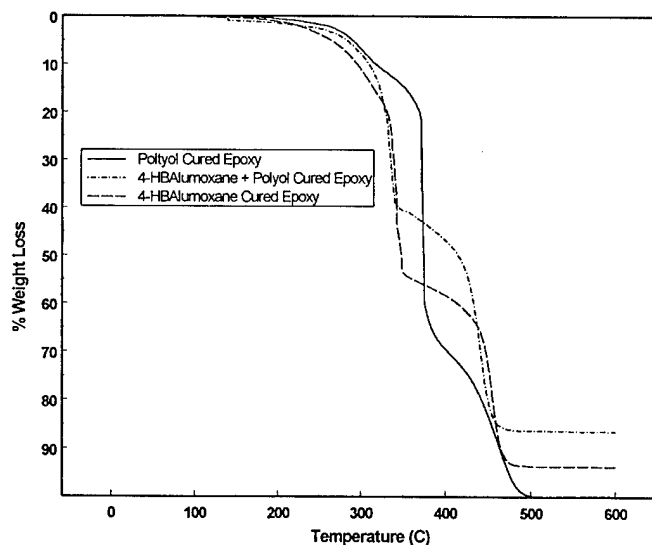


Figure 6. TGA of Epoxy and Composites.

addition of the alumoxane to the epoxy matrix significantly improves the dimensional stability of the epoxy at higher temperatures.

4.4.3. Thermo-mechanical Analysis

The thermo-mechanical behavior of the polyol cured epoxy and the HBA-alumoxane cured epoxy composite are shown in Figure 7. These results indicate that the epoxy-alumoxane composite materials are quite dimensionally stable at temperatures up to 300°C. Up to 300°C, the 4-HBA-alumoxane-epoxy composite material distorts by less than 1%, while the "pure" triol only cured epoxy has distorted by more than 2% at temperatures less than 100°C and by more than 5% at temperatures up to 300°C. Clearly the incorporation of the HBA-alumoxane into the polymer matrix results in a material with very good dimension stability. However, large painted aircraft aluminum panels undergo sizable dimensional changes on environmental heating and cooling. Aerospace coatings thus need to have sufficient flexibility to expand at a rate similar to that of the aluminum substrate. The coatings must also be flexible enough to withstand dimensional changes due to pressurization and wing movement. These needs suggest that we may need to add flexibility to the epoxy-alumoxane coatings to ensure that they do not crack (although the improved tensile strength of the materials allow use to have less flexibility than a weaker material).

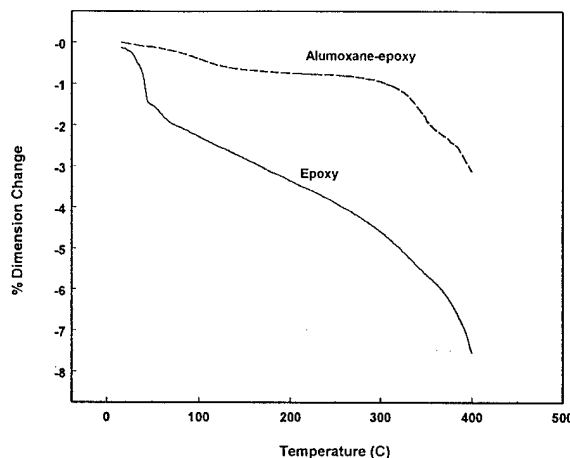


Figure 7. Thermo-mechanical testing of the HBA-containing composite coating materials.

4.4.4. Additional Research Efforts

Work is ongoing at Rice in the development of NMR methods to characterize the kinetics of the alumoxane-epoxy cure reactions. Both model and real systems are being studied. This may allow us to determine the relationship between the cure times and the cross-link density. Professor Barron's group is also carrying out FTIR studies to characterize the aluminum/alumoxane-epoxy interface. To get flat enough surfaces so that the FTIR result are meaningful, CVD deposited Al/Al₂O₃ thin films are being used as the substrate materials. Studies are underway to characterize Al - alumoxane interface.

With the ability to prepare larger batches of the alumoxane-epoxy precursors we can now supply reasonable quantities of the alumoxanes to University of Missouri-Rolla

(UMR) to carry out formulation of epoxy-alumoxane coatings and study their corrosion resistance. UMR is currently evaluating several alumoxane-epoxy precursors provided by TDA. Using feedback from UMR we will modify the precursors and forward the new materials to UMR for evaluation.

4.4.5. Anticipated Efforts for The Next Quarter

During the next quarter we will focus almost all of our efforts on formulation of alumoxane-epoxy mixtures and evaluation of their use as corrosion resistant coatings on aerospace aluminum substrates.

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